

Method for production and upgrading of oil

The field of the invention

The present invention relates to an environmental-friendly, integrated process for increased production and upgrading/refining of heavy and extra-heavy crude oil to finished products, based on extensive use of hydrogen to maximise the yield of liquid products, while cogenerating large amounts of steam, CO₂ and optionally N₂ produced by large-scale natural gas conversion, used for increased oil production. The finished products from upgrading/refining of heavy/extra heavy oils will be predominantly naphtha, kerosene, diesel and fuel oil, shipped separately or blended.

The background of the invention

Compared to conventional oil, the utilization of heavy oil (density<20°API, viscosity >100cP) and extra heavy oil/bitumen (density<10°API, viscosity>10000cP) is limited because of cost of production and upgrading. However, it is expected that the continued need for petroleum liquids such as transportation fuels will be met in the future more and more by heavy oils. Hence new technologies for increased production and more efficient upgrading/refining of heavy and extra heavy oil are much sought for. Due to its high viscosity the primary recovery of heavy oils by conventional methods is low. Recent developments in production technology, such as horizontal drilling, gravity drainage methods, non-thermal production from horizontal wells with multilaterals, cold production of heavy oil with sand co-production, pressure pulse flow enhancement are methods which can increase the recovery of heavy oils at a reasonable cost. In particular, improvements in cyclic steam stimulation (CSS) and steam assisted gravity drainage (SAGD) have reduced the cost of those hot production methods, but still they require large amounts of steam (volumetric steam-to-oil ratios of 2 or higher) .

Today, heavy and extra-heavy oil are converted to finished products in two steps, where the first step referred to as upgrading gives a synthetic crude oil which has to be further refined to finished products. The upgrader is usually designed for the specific heavy oil in question, while the synthetic crude with API in the range of typically 20-35 API is an attractive feedstock for conventional refineries, within certain limitations. The essential feature of the heavy/extra heavy oil upgrader will be the conversion of residue, either by carbon rejection or hydrogen addition, to give a stable synthetic crude that might be more or less residue-free, while the liquid fractions do not have the quality needed for

road transportation fuels. A subsequent refining of the synthetic crude is needed to produce finished products with the right quality, but this reprocessing is not very energy efficient since the synthetic crude oil has to be reheated and fractionated.

- 5 The heavy oils generally have high density and high viscosity due to the large presence of higher boiling, polyaromatic molecules in which the resin and asphaltene content can be as high as 70%. As a result, these oils are low in hydrogen content, such as for Athabasca bitumen with an ratio (atomic) H/C equal to 1.49, compared to conventional
10 the most important refinery products, gasoline and diesel (see, J. S. Speight: "The chemistry and technology of petroleum", 3rd ed., Marcel Dekker, Inc., New York, 1999).

Hence, to produce valuable liquid products in high quantities, substantial amounts of
15 hydrogen will be needed, and more so the heavier the crude oil. In comparison, natural gas is rich in hydrogen with a H/C-ratio around 3.8; therefore natural gas represents a natural source of hydrogen for upgrading of heavy oil, as it is when refineries need additional hydrogen to close their hydrogen balance. The attractiveness of using natural gas as hydrogen source will depend on local factors such as availability and cost of the
20 natural gas.

The need for hydrogen in the refineries depends on the feedstock and product slates, as well as the specific refinery configuration. The general market trend is towards lighter products such as LPG, naphtha, gasoline and diesel, putting a pressure on the refineries
25 with respect to upgrading of the heavier fractions. Moreover, new specification on the sulfur content in transportation fuels normally requires increased hydrotreating in the refineries, a type of processing that consumes hydrogen, thereby contributing to a hydrogen imbalance in the refineries.

- 30 Upgrading of the heavier fractions can be done either by "carbon-rejection" type of processes such as delayed coking or catalytic cracking, or by hydrogen addition such as hydrocracking. The former produces "coke" which is burnt as energy input in the

processing/upgrading or sold as a product (petroleum coke), while the latter gives a higher yield of high-value liquid products of the kind mentioned above, at the penalty of higher hydrogen consumption.

- 5 The particular high content of residue in heavy oils requires particular refinery configurations to process these crudes, and the high content of metals and carbon residue/asphaltenes in the residue limits the use of catalytic processes available to upgrade the heavy ends of those heavy crudes. The hydrocracking option allows for production of ultra-clean (low sulfur) transportation fuels of a quality in compliance with the most stringent fuel specifications both in EU and in the US. This will normally require a two-step hydrocracking scheme, where the products from the residue hydrocracker must be hydrocracked in a VGO type of hydrocracker to give the ultra-clean transportation fuels.
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- 15 In catalytic hydrocracking of residue, the metals will end up on the catalyst, which by proper treatment can be dissolved and the metals, mainly Vanadium and Nickel, recuperated. The sulfur ends up as H₂S which is easily captured and for example converted to elementary sulfur by use of techniques commonly used in refineries today. Thus, the inherent high content of impurities such as metals and sulfur in the heavy oil, will be properly handed in the upgrader.
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Today, the change in demand pattern has created regional lack of sufficient upgrading capacity in the refining industry, the so-called bottom-of-the-barrel problem. This, combined with limited hydrogen availability, will probably make it less attractive for conventional refineries to process heavier crudes.

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Heavy oils are, due to their physical properties and particularly the high viscosity, difficult to produce and transport. Technologies have been developed for partial upgrading at the wellhead to make the oil transportable, as an alternative to dilution of the viscous oil by lighter fractions such as typically naphtha. The common solution for the Orinoco bitumen produced in Venezuela is transport by pipeline by naphtha dilution to an upgrader located at the coast, where the naphtha is separated from and recycled, while the crude is partially upgraded to an essentially residue-free synthetic crude with

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densities in the range of typically 20-32API. The synthetic crude is then exported to a conventional refinery for upgrading to finished products.

- 5 As an alternative to this conventional two-step upgrading of heavy oil, we see potential advantages at locations where natural gas can be made available in large quantities, to profit from large scale hydrogen production from natural gas, by upgrading the heavy or extra-heavy crude oil to products in one step at a dedicated upgrader/refinery located so as to obtain maximum synergetic effects with the hydrogen production, which will take place so as to also obtain synergetic effects with respect to improved recovery of heavy or extra-heavy oil from the reservoir, by the use of energy such as steam in combination with by-products such as CO₂ and/or N₂, generated by the natural gas conversion step. The amount of hydrogen required of course depends on the characteristics of the heavy oil, the upgrader/refinery scheme and the types of products, but a simple mass balance demonstrates that production of finished products from an extra-heavy oil requires so much hydrogen that it could possibly serve as a single solution for remote or stranded gas which then must be transported to (or close to) the heavy oil production site. In some cases, the natural gas could even be available as associated gas, produced with the oil.
- 10 20 Due to its high viscosity the primary recovery of heavy oils by conventional methods is low. Recent developments in production technology, such as horizontal drilling, gravity drainage methods, non-thermal production from horizontal wells with multilaterals, cold production of heavy oil with sand co-production, pressure pulse flow enhancement are methods which can increase the recovery of heavy oils at a reasonable cost.
- 25 30 The reinjection of various gases into an oil reservoir in order to enhance the oil recovery from the reservoir, and to stabilise it, has long been known and used. In particular, improvements in cyclic steam stimulation (CSS) and steam assisted gravity drainage (SAGD) have reduced the cost of those hot production methods, but still they require large amounts of steam (volumetric steam-to-oil ratios of 2 or higher) . Gases such as CO₂, N₂ and natural gas will reduce the surface tension between gas and oil, and thus contribute to both increased recovery and stabilisation of the reservoir. Additionally, natural gas as such may be injected into fields where the gas does not have a net value that exceeds the excess profits of increasing the oil recovery in the field.
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WO03/018958 relates to a combined facility for production of gases for injection into an oil field and production of synthesis gas for synthesis of methanol or other oxygenated hydrocarbons or higher hydrocarbons in a synthesis loop.

- 5 Introduction of gases as mentioned above is not sufficient to produce and transport heavy oil and extra heavy oil /bitumen even if oil soluble gases like e.g. CO₂ and methane will, dependent on the pressure and temperature of the mixture, reduce the viscosity somewhat.
- 10 An integrated process for gas conversion and bitumen production is described in WO02/077124. Synthesis gas, comprising a mixture of H₂ and CO is produced from hydrocarbons, preferably from natural gas. The natural gas may be found in the same formations as the heavy oil or in nearby the heavy oil reservoir. Heat from the synthesis gas production is used to produce steam for injection into the formation to lower the
- 15 viscosity of the heavy oil by heating it. The synthesis gas is used to produce hydrocarbons by use of a Fischer-Tropsch catalyst. At least a part of the produced hydrocarbons is used to dilute the produced heavy hydrocarbons to lower the viscosity to facilitate the transportation of the oil in pipelines.
- 20 US 4.706.751 describes another heavy oil recovery process for the recovery of heavy oils from deep reservoirs. Reactant streams are produced in a surface process unit. The reactant streams, that may be e.g. H₂ and O₂ plus water, or CO and steam plus water, is introduced into the well and reacted in a catalytic reactor downhole to produce high quality steam, H₂, CO₂ and any gas or vapour that are readily soluble in the heavy oil
- 25 such as methane, methanol, light hydrocarbons etc. The reactions in the downhole reactor are exothermal and produce heat for steam formation and heating.

Cleaning waste gas from the combustion on the production installation can provide CO₂ for injection into oil reservoirs. In addition it has been suggested that CO₂ cleaned from

30 the flue gas from gas power plants be reinjected by laying a pipeline from a gas power plant to the production installation for hydrocarbons.

The present invention aims at combining various elements of known methods of natural gas conversion and heavy oil upgrading by upgrading of the heavy/extra heavy oil to high value, finished products by the use of large amounts of hydrogen generated from the natural gas. As byproducts we obtain steam, CO₂, water and optionally N₂, which
5 can be used for enhanced recovery of the heavy oils from the reservoir. In particular, the capture of CO₂ from the hydrogen generation plant represents a significant potential of reduction of the CO₂ emissions from the upgrading by injection of the CO₂ into underground storage (sequestering), or injection into to reservoir to obtain enhanced oil recovery.

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Summary of the invention

According to the present invention there is provided an integrated process for production and upgrading of heavy and extra-heavy crude oil, comprising (a) reforming of natural gas to produce hydrogen, CO₂ and steam (b) separating the produced
15 hydrogen from the CO₂, steam and any other gases to give a hydrogen rich fraction and a CO₂ rich fraction and steam, (c) injecting the steam alone or in combination with the CO₂ rich fraction into the reservoir containing heavy or extra heavy oil to increase the oil recovery, and (d) upgrading/refining of the heavy or extra heavy oil by hydroprocessing , comprising hydrocracking and hydrotreating using the hydrogen rich
20 fraction in the hydroprocessing steps. The term "hydrotreating" comprises, as used in the present invention, removal of sulfur, nitrogen and metals as well as hydrogenation of olefins and aromatics.

According to a preferred embodiment the reforming in step (a) is steam reforming.

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The steam reforming may be performed under supercritical conditions.

According to another preferred embodiment the reforming in step (a) is autothermal reforming or partial oxidation.

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Air may be used as oxidizer in the autothermal reformer or in the partial oxidation reactor.

Preferably the process comprises the additional step of air separation to produce purified oxygen comprising more than 95%, preferably more than 98% oxygen, that is used as oxidizer in the reforming. The use of purified oxygen in the reforming and separation of the reformed gases, reduces the gas volume in the reactors and the separation units. Accordingly the volume and building costs may be reduced and the separation of hydrogen from the remaining gases is more effective.

Preferably, purified nitrogen co-produced with the purified oxygen is injected into the reservoir together with the CO₂ rich fraction in step (c) to stimulate the oil production. Nitrogen is effective as pressure support in the reservoir together with the CO₂ rich fraction. It is therefore cost effective to use the produced purified nitrogen for injection.

The process according to any of the preceding claims, wherein CO produced during the reforming process is reacted in a water gas shift reaction to produce additional CO₂ and H₂.

The reformed gas from steam reforming, partial combustion or autothermal reforming comprises CO. The CO is therefore preferably converted by a water gas shift reaction to produce additional CO₂ and H₂.

According to a preferred embodiment the heavy or extra heavy oil is partially upgraded in the reservoir by hydrogen injection.

According to a preferred embodiment the heavy or extra heavy oil is partially upgraded in a downhole upgrading unit.

Partial upgrading of the heavy or extra heavy oil in the reservoir makes the oil less viscous. Upgrading in the reservoir may therefore increase the oil production, whereas both upgrading in the reservoir and in a downhole unit will improve the transportability of the oil

It is preferred that the heavy or extra heavy oil is upgraded on an offshore or onshore upgrading facility.

According to a preferred embodiment at least a part of the heat to increase recovery of the heavy or extra heavy oil is generated by in-situ combustion.

- 5 According to an embodiment geothermal heat is used to increase recovery and transport of the heavy or extra heavy oil.

As an alternative to traditional two-step upgrading of heavy oil (via synthetic crude), a potential advantages is seen at locations where natural gas can be made available in
10 large quantities, to profit from large scale hydrogen production from natural gas, by upgrading/refining the heavy or extra-heavy crude oil to finished products in one step at a dedicated upgrader/refinery located so as to obtain maximum synergetic effects with the hydrogen production, which will take place so as to also obtain synergetic effects with respect to improved recovery of heavy or extra-heavy oil from the reservoir, by the
15 use of energy such as steam in combination with by-products such as CO₂ and/or N₂, generated by the natural gas conversion step.

20 **Brief description of the drawings**

Figure 1 is a flowchart illustrating a first preferred embodiment, and
Figure 2 is a flowchart illustrating a second preferred embodiment.

25 **Detailed description of the invention**

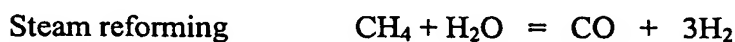
The present invention will be described by means of two examples describing two preferred embodiments of the invention. According to the present invention gas and optionally heat as steam for injection into an oil field

30 **Example 1 – Generation of hydrogen by steam reforming of natural gas**

Figure 1 is a simplified flow diagram of a plant according to a first preferred embodiment and is based on the production of 200 000 barrels per day of Zuata Heavy (API=9) oil.

- 5 Natural gas, 115 ton per hour, is introduced into a steam reforming unit 2 via a gas line 1. Steam reforming is an endothermal reaction. The steam reforming unit comprises a conventional steam generation unit where water is heated and converted into hot steam by combustion of any suitable fuel such as natural gas, lower or higher hydrocarbons.

- 10 The natural gas from the gas line 1 and the hot steam is reacted in one or more reactors according to the following reactions:



- 15 The product gas from the steam reformer is then sent to a shift converter (one or two step) in which CO is converted to CO₂ by the water gas shift reaction, and hydrogen is then separated by means of well known separation techniques, such as membrane separation or separation by absorption based on the different chemical properties of gases e.g. as described in WO00/18681, into a hydrogen rich fraction leaving the steam reformation unit 2 through a hydrogen line 3 and a fraction comprising mainly CO₂ and steam leaving the unit through line 4. The hydrogen rich fraction in line 3 constitutes about 35 ton per hour, whereas about 300 ton CO₂ per hour and 210 ton steam per hour leaves the unit through line 4. This concept represents a favourable way of CO₂ capture due to the high concentration of the CO₂ in the process stream.

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The preparation of a H₂ rich gas and a CO₂ rich gas may be performed high pressure at supercritical conditions as described in WO/00/18681.

- 30 The CO₂ and steam is led to a unit for heavy oil production 5 and injected to enhance the recovery of heavy oil. Heavy oil produced in the unit for heavy oil production 5 is led from the unit to a unit for heavy oil upgrading 7 through a heavy oil line 6.

The heavy oil is upgraded by several steps of catalytic hydroprocessing of the heavy or extra heavy oil using hydrogen from line 3, by hydrocracking in combination with hydrotreating steps, to produce valuable liquid products (distillates) from the
 5 distillation residue, to saturate unsaturated hydrocarbons and to remove asphaltenes, metals, nitrogen and sulphur from the finished products.

The products from the heavy oil upgrading unit 7 leaves the unit through a plurality of lines 8. Table 1 indicates a typical yield structure from the unit 7.

10 Table 1

Product	Ton per hour	C-range
Naphtha	200	C5-C8
Kerosine	140	C8-C12
Diesel	580	C12-C22
VGO	300	C22 - 380C
Fuel oil , sulphur	60	380 C +

Example 2 – Generation of hydrogen by autothermal reforming of natural gas

Figure 2 illustrates a second preferred embodiment of the present invention, where
 15 hydrogen for the heavy oil upgrading and gas for injection into the reservoir is generated by autothermal reforming (ATR) of natural gas. The example is based on the same heavy oil and production volume of oil as Example 1.

Natural gas, 135 ton per hour (221.000 Sm³ per hour), is introduced through a gas line
 20 10 and O₂ (from an air separation unit) is introduced through a line 10' into an ATR unit 11. The ATR unit 11 comprises one or more autothermal reforming reactors wherein natural gas is reformed by steam reforming combined with partial combustion. Steam reforming is, as mentioned above, an endothermal reaction and the energy required is supplied from partial combustion of a part of the natural gas in the same reactor
 25 according to the following reactions:

Steam reforming $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$

Partial combustion $\text{CH}_4 + \frac{3}{2} \text{O}_2 = \text{CO} + 2\text{H}_2\text{O}$

The CO is thereafter converted into CO_2 according the following reaction:

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Water gas shift $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

Hydrogen, 35 ton per hour, is separated from the remaining gases as described in example 1 and a hydrogen rich fraction is led into a hydrogen line 12 to a heavy oil upgrading unit 17.

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Oxygen for the partial combustion is preferably introduced into the reactor(s) as purified oxygen or oxygen enriched air. Purified oxygen is preferred as the absence of the inert nitrogen in the reactor reduces the total gas in the system and simplifies the separation of hydrogen. The purified oxygen is generated in an air separation unit (ASU), separating oxygen and nitrogen in two fractions.

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The nitrogen, 4.1 GSm³/y, from the ASU is led through a nitrogen line 13 and CO_2 , 350 ton per hour from the ATR unit 11 is led through a line 14 to a unit for heavy oil production 15. The steam amount available for injection is the difference between the steam produced in the synthesis gas heat recovery section and the steam needed for production of 70 MW power for the ASU. In the unit for heavy oil production the nitrogen, CO_2 and steam are injected to enhance the recovery of heavy oil. Heavy oil produced in the unit for heavy oil production 15 is led from the unit to a unit for heavy oil upgrading 17 through a heavy oil line 16. The products from the unit for heavy oil upgrading correspond to the products described in Example 1.

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Calculations have been carried out for a plant, according to Figure 2, for production of hydrogen by Auto-Thermal Reforming (ATR) of natural gas. The hydrogen consumption will be about 35 ton/hr (410500 Sm³/hr) for upgrading 200000 bpd heavy oil. The natural gas needed for production of this amount of H_2 will be about 1.75 GSm³/year depending on of much flue gas and LPG that are available in the integrated

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natural gas and heavy oil upgrading complex. In this example no flue gas or LPG are used as feed to the reforming section. By partly replacing the natural gas feed with flue gas and LPG the natural gas consumption may be decreased by more than 20 %.

- 5 The air separation unit can deliver 23040 MTPD N₂ and 3840 MTPD O₂. This air separation unit requires approximately 70 MW of power, which is delivered in the form of high-pressure steam from the synthesis gas section. The ratio between O₂ and natural gas will be about 0.65 giving a nitrogen production of about 4.1 GSm³/year (2.34*1.75 GSm³/year)

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The nitrogen is extracted at 3 bar and 0 degrees C. The gas is compressed to 220 bars for injection (IOR). Compression requires approximately 180 MW.

- 15 The oxygen is fed to an ATR for production of synthesis gas from natural gas. The process operates with a steam/carbon ratio of 0.6. The temperature and pressure at the outlet from the ATR is 1030 degrees Celsius and 45 bars respectively. See Table 2 for the natural gas composition. Note! All compositions are given on a dry basis, i.e. without water.

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	Natural gas	Oxygen
	Mole %	Mole %
CH ₄	83.7	
C ₂ H ₆	5.2	
C ₃₊	3.2	
CO ₂	5.2	
N ₂ + Ar	2.7	1.0
O ₂	0.0	99.0
H ₂ O	0.0	
Sum	100	
Total [Sm ³ /hr]	221 000	190 850

Table 2. Composition of feeds to synthesis gas section

	ATR outlet
	Mole %
H ₂	62.9
CO	28.5

CO ₂	4.8
CH ₄	2.5
N ₂ + Ar	1.3
Sum	100
Total [Sm ³ /hr]	652000

Table 3. Gas composition out of the ATR

The synthesis gas is further sent to CO shift conversion. The gas mixture into the shift reactor can have a varying composition depending on the conditions in the ATR (steam ratio, pressure and temperature). One-step shift reactor may convert the CO down to a few percent. A two-step shift converter may decrease the CO content in the gas far below 1 percent. The gas mixture out from the shift reactor contains significant amounts of steam. After cooling to e.g. 40 °C most of the steam will be condensed out.

The separation of CO₂ may be performed by amine washing (e.g. ethanol amine) capturing above 90 % of the CO₂ in the gas. The CO₂ rich amine solution is fed to a stripping unit where the CO₂ will be liberated because of the temperature increase and pressure reduction, further CO₂ can be set free from the amine solution by stripping with steam.

99% of the CO₂ in the gas (equivalent to 330 ton CO₂ per hour) is recovered in an MDEA process. Due to a high concentration of CO₂ in the natural gas feed, this example includes CO₂ removal prior to ATR (equivalent to 20 ton CO₂ per hour), so that the total amount of recovered CO₂ is 350 ton per hour. Recovered CO₂ is compressed to 220 bar, and may if so desired be mixed with nitrogen (and eventually available steam) prior to injection into the reservoir. This concept also represents a favourable way of CO₂ capture due to the high concentration of the CO₂ in the process stream.

The remaining gas is used in fired heaters for superheating of steam in power production and preheating of natural gas feeds.

The unit for heavy oil upgrading/refining may in both examples one can envisage use the gases produced in the present concept for both downhole upgrading and enhanced

oil recovery. Hydrogen could be used for partial downhole upgrading to obtain a transportable oil which would be upgraded to finished products at a nearby upgrader or exported to another refinery. A downhole unit will reduce the loss of energy (heat) in transport lines of steam, gases and oil. Additionally, dilution of the heavy oil to make it
5 flow through transport lines will be unnecessary.

The energy needed to increase the transportability of the heavy oil in the reservoir may also be geo heat or a combination of geo heat and energy produced in the reforming process both down hole and in more conventional facilities off- or onshore.

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It is also possible to supply heat to a reservoir by injection air, oxygen or oxygen enriched air into the reservoir. For reservoir temperatures above about 50 °C, spontaneous combustion will usually occur soon after the start of air injection. The heat produced by the combustion will, if the temperature of the combustion is high enough,
15 vaporize the water and some of the oil to enhance the recovery of oil from the reservoir.

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Any hydrogen produced in the gas conversion part, i.e. ATR or steam reforming units, can be used for other purposes, such as fuel for fuel cells, and for other industrial purposes such as production of ammonia, methanol and synthetic fuel.